



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>H01L 51/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/42668</b> <b>(43) International Publication Date:</b> 20 July 2000 (20.07.00)
<b>(21) International Application Number:</b> PCT/US99/30612 <b>(22) International Filing Date:</b> 22 December 1999 (22.12.99) <b>(30) Priority Data:</b> 60/116,112 15 January 1999 (15.01.99) US <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). <b>(72) Inventors:</b> BERNIUS, Mark, T.; 401 Mayfield Lane, Midland, MI 48640 (US). WOO, Edmund, P.; 300 Mayfield Lane, Midland, MI 48640 (US). <b>(74) Agent:</b> ZERULL, Susan, Moeller; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> CA, CN, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SEMICONDUCTING POLYMER FIELD EFFECT TRANSISTOR		
<b>(57) Abstract</b> <p>A field effect transistor is made of five parts. The first part is an insulator layer, the insulator layer being an electrical insulator such as silica, the insulator layer having a first side and a second side. The second part is a gate, the gate being an electrical conductor such as silver, the gate being positioned on the first side of the insulator layer. The third part is a semiconductor layer, the semiconductor layer including a polymer, at least ten weight percent of the monomer units of the polymer being a 9-substituted fluorene unit and/or a 9,9-substituted fluorene unit, the semiconductor layer having a first side, a second side, a first end and a second end, the second side of the semiconductor layer being on the second side of the insulator layer. The fourth part is a source, the source being an electrical conductor such as silver, the source being in electrical contact with the first end of the semiconductor layer. The fifth part is a drain, the drain being an electrical conductor such as silver, the drain being in electrical contact with the second end of the semiconductor layer. A negative voltage bias applied to the gate causes the formation of a conduction channel in the semiconductor layer from the source to the drain. On the other hand, a positive bias applied to the gate causes the formation of an electron conducting channel in the semiconductor layer.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## SEMICONDUCTING POLYMER FIELD EFFECT TRANSISTOR

This application claims the benefit of U.S. Provisional Application Serial No. 60/116,112, filed January 15, 1999.

The instant invention is in the field of transistors. More specifically, the instant invention is in the field of transistors based on semiconducting polymers.

Transistors are important electronic devices. Metal oxide semiconductor field effect transistors (MOS FET) are well-known.

A field effect transistor comprises five elements. The first element is an insulator layer, the insulator layer being an electrical insulator, the insulator layer having a first side and a second side. The second element is a gate, the gate being an electrical conductor, the gate being positioned adjacent the first side of the insulator layer. The third element is a semiconductor layer, the semiconductor layer comprising a polymer, at least ten weight percent of the monomer units of the polymer being selected from a 9-substituted fluorene unit and a 9,9-substituted fluorene unit, the semiconductor layer having a first side, a second side, a first end and a second end, the second side of the semiconductor layer being adjacent the second side of the insulator layer. The fourth element is a source, the source being an electrical conductor, the source being in electrical contact with the first end of the semiconductor layer. The fifth element is a drain, the drain being an electrical conductor, the drain being in electrical contact with the second end of the semiconductor layer. A negative voltage bias applied to the gate causes the formation of a hole conduction channel in the semiconductor layer connecting the source to the drain. A positive bias applied to the gate causes the formation of an electron-conducting channel in the semiconductor layer.

Fig. 1 is a cross-sectional side view of an embodiment of the instant invention.

The instant invention is termed herein as a "metal-insulator-semiconductor field effect transistor" (MISFET). The MISFET comprises a semiconductor layer adjacent an insulator layer. Two electrodes (source and drain) are attached to the semiconductor layer and a third electrode (gate) is positioned adjacent the other side of the insulator layer. The semiconductor layer comprises a polymer. At least ten weight percent of the monomer units of the polymer are selected a 9-substituted fluorene unit and a 9,9-substituted fluorene unit. In a p-type field effect transistor, applying a negative DC voltage to the gate electrode induces an accumulation of "holes" near the insulator side of the semiconductor layer, creating a conduction channel through which electric current can flow by hole transport between the source and the drain so that the MISFET is in the "on" state. Zeroing the gate voltage causes

a depletion of holes in the accumulation zone and cessation of current so that the MISFET is in the "off" state. The speed at which the MISFET can be turned on and off depends on the speed at which "holes" can travel from the source to the drain and, thus, on the mobility of the "holes". On the other hand, in an n-type field effect transistor, a positive bias applied to the gate causes the formation of an electron-conducting channel in the semiconductor layer.

Referring now to Fig. 1, therein is shown a side cross-sectional view of an apparatus embodiment 10 of the instant invention. The embodiment 10 comprises an insulator layer 11, the insulator layer 11 being an electrical insulator, the insulator layer 11 having a first side 12 and a second side 13. The embodiment 10 also comprises a gate 14, the gate 14 being an electrical conductor, the gate 14 being positioned adjacent (and preferably in contact with) the first side 12 of the insulator layer 11. The embodiment 10 also comprises a semiconductor layer 15, the semiconductor layer 15 comprising a polymer, at least ten weight percent of the monomer units of the polymer being selected from a 9-substituted fluorene unit and a 9,9-substituted fluorene unit, the semiconductor layer 15 having a first side 16, a second side 17, a first end 18 and a second end 19, the second side 17 of the semiconductor layer being adjacent (and preferably in contact with) the second side 13 of the insulator layer. The embodiment 10 also comprises a source 20, the source 20 being an electrical conductor, the source 20 being in electrical contact with the first end 18 of the semiconductor layer 15. The embodiment 10 also comprises a drain 21, the drain 21 being an electrical conductor, the drain 21 being in electrical contact with the second end 19 of the semiconductor layer 15. Electrical connection to the embodiment 10 is by way of electrical leads 22, 23 and 24 to the gate 14, the source 20 and the drain 21, respectively. The embodiment 10 also is shown as including an optional substrate 25 which serves as a structural base for the embodiment 10.

Referring still to Fig. 1, the embodiment 10 can be made by the following steps. First, the gate 14 is formed onto the substrate 25. The substrate 25 may be chosen from a variety of materials including silicon wafers, glass, or plastics. The gate 14 may be formed from any conductive material (usually a metal such as silver, gold or aluminum but conductive non-metals can be used such as indium tin oxide or a heavily doped silicon). The gate 14 may be formed by any standard technique including ion implantation for doped silicon, thermal evaporation in vacuum or sputtering for metals, preferably through an appropriate mask. Alternatively, the substrate 25 may be eliminated by forming the gate 14 from a sufficiently thick conductive material such as an aluminum disk.

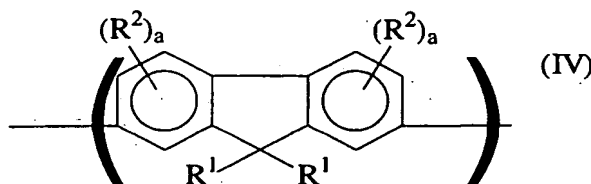
The insulator layer 11 is then formed onto the gate 14. The material for the insulator layer 11 is preferred to have a dielectric constant of at least 3 and may be a polymer

(for example, polyimides, poly(methylmethacrylate), polysulfene, etc.), an inorganic oxide (for example, GeO, CaO, SiO, MgO, SiO<sub>2</sub>, SnO, SnO<sub>2</sub>), an inorganic fluoride (for example, CsF, CaF<sub>2</sub>, MgF<sub>2</sub>, LiF), and an inorganic nitride (for example, Si<sub>3</sub>N<sub>4</sub>). The thickness of the insulator layer 11 is most preferably as thin as possible while maintaining electrical insulation between the gate 14 and the semiconductor layer 15 within the voltage rating of the embodiment 10.

The semiconductor layer 15 is then formed onto the insulating layer by, for example, standard solution processes. The semiconductor layer 15 comprises a polymer. At least ten weight percent (preferably at least 20 weight percent and more preferably at least 30 weight percent) of the monomer units of the polymer being selected from a 9-substituted fluorene unit and a 9,9-substituted fluorene unit.

Examples of such polymers are described in United States Patent 5,708,130; United States Patent 5,777,070, United States Patent Application Serial Number 08/861,469 filed May 21, 1997; United States Patent 5,962,631; and WO99/54385.

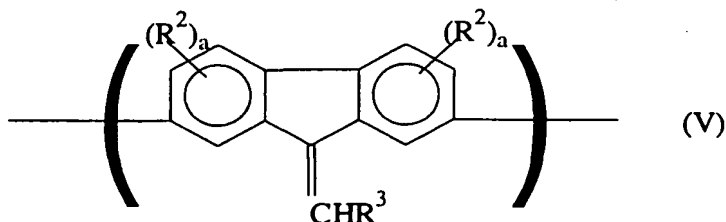
Specifically, the polymers, preferably, have groups of the formula



wherein R¹ is independently in each occurrence C<sub>1-20</sub> hydrocarbyl or C<sub>1-20</sub> hydrocarbyl containing one or more S, N, O, P or Si atoms, C<sub>4-16</sub> hydrocarbyl carbonyloxy, C<sub>4-16</sub> aryl(trialkylsiloxy) or both R¹ may form with the 9-carbon on the fluorene ring a C<sub>5-20</sub> ring structure or a C<sub>4-20</sub> ring structure containing one or more heteroatoms of S, N or O;

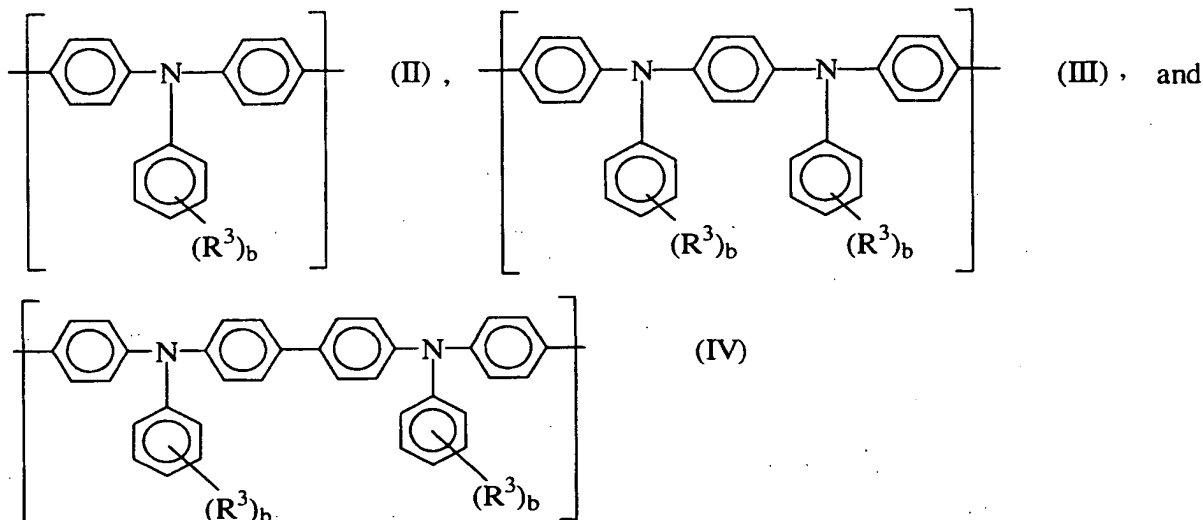
R² is independently in each occurrence C<sub>1-20</sub> hydrocarbyl, C<sub>1-20</sub> hydrocarbyloxy, C<sub>1-20</sub> thioether, C<sub>1-20</sub> hydrocarbylcarbonyloxy or cyano and

A is independently in each occurrence 0 or 1; and/or groups of the formula:



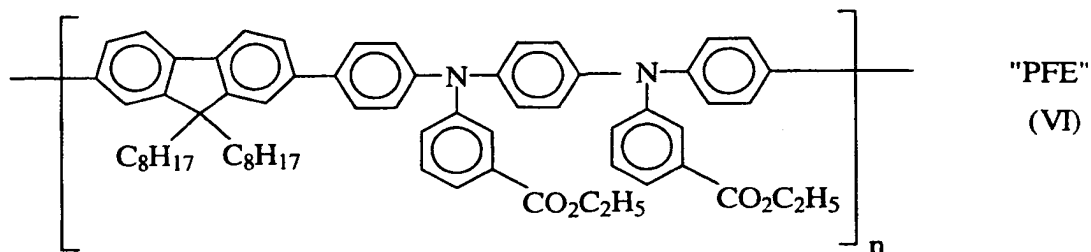
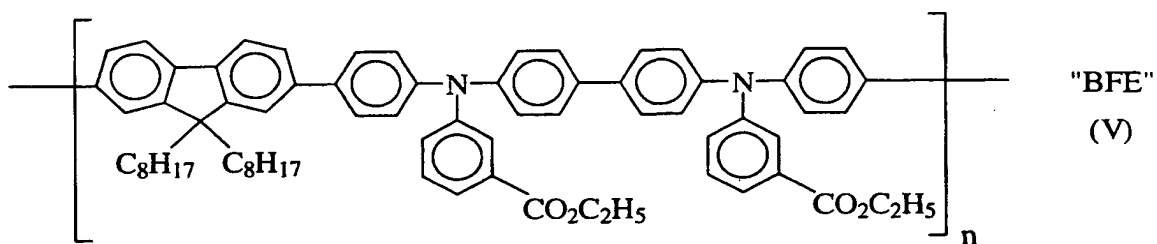
wherein  $R^2$  and  $a$  are as defined above, and  $R^3$  is independently in each occurrence  $C_{1-20}$  hydrocarbyl or  $C_{1-20}$  hydrocarbyl substituted with di( $C_{1-20}$  alkyl)amino,  $C_{1-20}$  hydrocarbyloxy or  $C_{1-20}$  hydrocarbyl or tri( $C_{1-10}$  alkyl)siloxy.

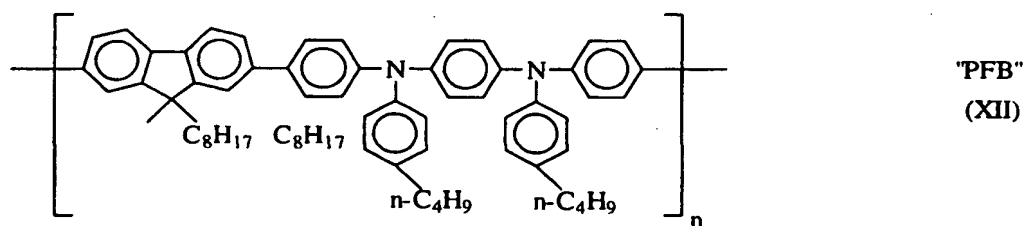
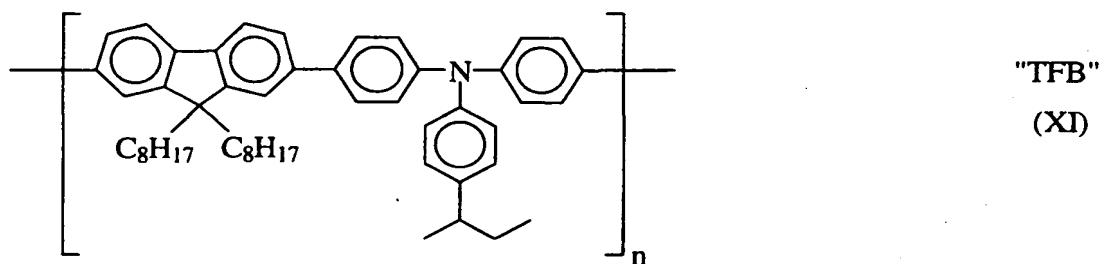
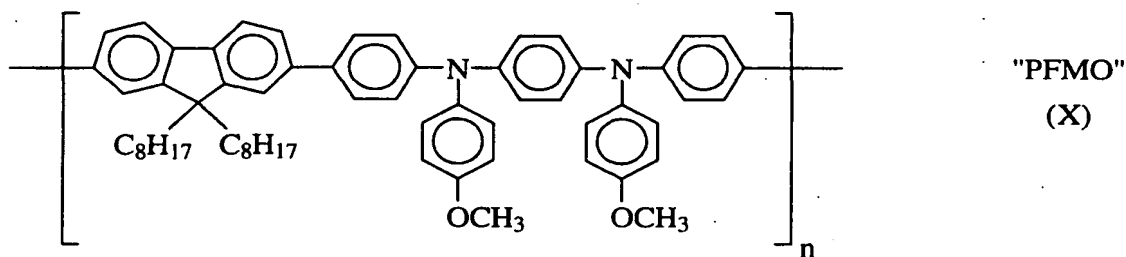
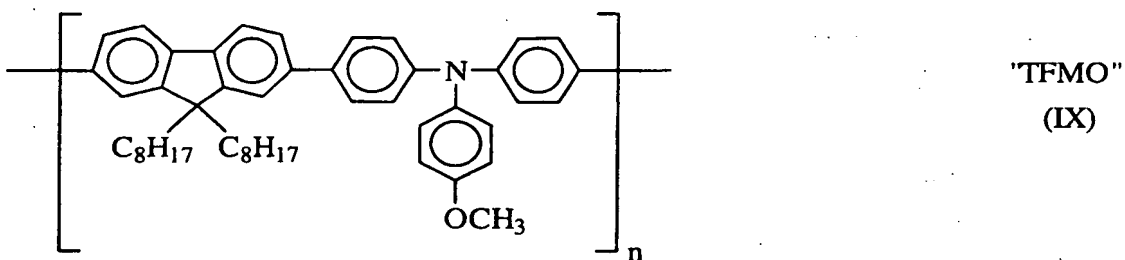
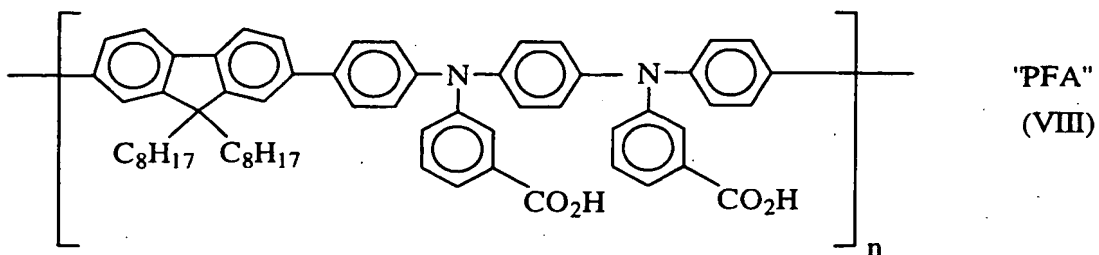
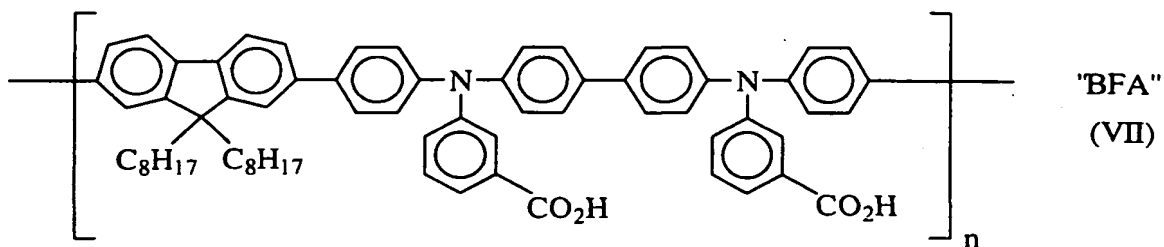
Comonomeric groups that may be used include:



$R^3$  is independently in each occurrence carboxyl,  $C_1$ - $C_{20}$  alkyl,  $C_1$ - $C_{20}$  alkoxy or a group of the formula  $-CO_2R^4$  wherein  $R^4$  is a  $C_1$ - $C_{20}$  alkyl; and

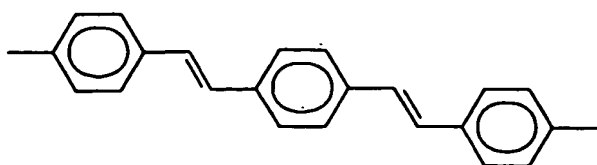
$b$  is independently in each occurrence an integer from 0 to 3. Examples of such copolymers include:



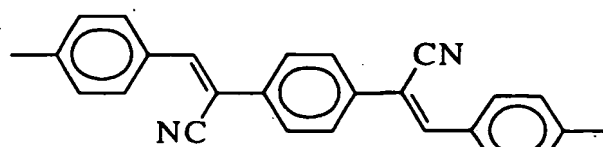


Other comonomeric groups include stilbene, tolan, C<sub>6</sub>-C<sub>20</sub> mononuclear/polynuclear aromatic hydrocarbons, and C<sub>2</sub>-C<sub>10</sub> mononuclear/polynuclear heterocycles. Examples of mononuclear/polynuclear aromatic hydrocarbons include benzene, naphthalene, acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, rubrene, and chrysene. Examples of mononuclear/polynuclear heterocycles include 5-member heterocycles such as furan, thiophene, pyrrole, oxazole, isooxazole, thiazole, isothiazole, imidazole, oxadiazoles, thiadiazole, and pyrazoles; 6-member heterocycles such as pyridine, pyridazine, pyrimidine, pyrazine, triazines, and tetrazines; benzo-fused ring systems such as benzoxazole, benzothiazole, benzimidazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, phthalazine, benzothiadiazole, and benzotriazines; and polynuclear condensed ring systems such as phenazine, phenanthridine, acridine, carbazole, and diphenylene oxide. In general, conjugated compounds containing up to 30 carbons are useful for the present purpose. They may be substituted optionally with one or more substituents that are not deleterious to the photoluminescent properties of the polymer compositions. Examples of substituents include C<sub>1</sub>-C<sub>20</sub> hydrocarbyl radicals, C<sub>1</sub>-C<sub>20</sub> (thio)alkoxy radicals, C<sub>1</sub>-C<sub>20</sub> (thio)aryloxy radicals, cyano, fluoro, chloro, C<sub>1</sub>-C<sub>20</sub> alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> aryoxycarbonyl, C<sub>1</sub>-C<sub>20</sub> carboxyl, and alkyl(aryl)sulfonyl radicals. Substituents which are known photoluminescent quenchers, such as arylcarbonyl and nitro, are undesirable. Conjugated monomeric units of more complex structures, as exemplified by Structures (1) - (8), may also be used.

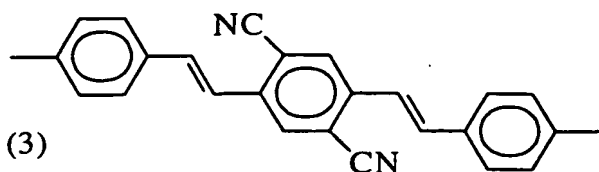




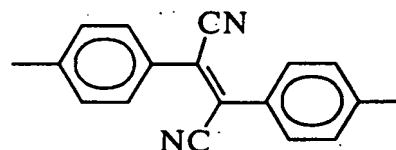
(1)



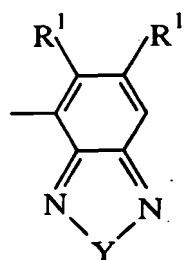
(2)



(3)

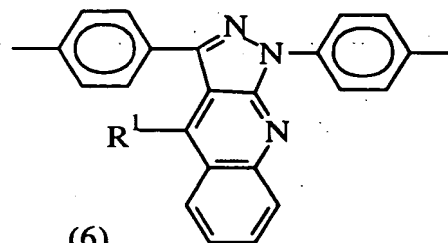


(4)

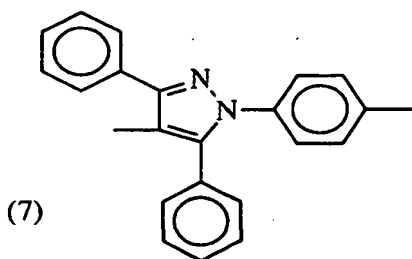


(5)

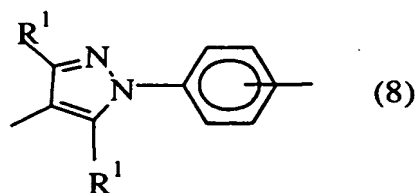
Y = S or O



(6)



(7)



(8)

Preferred fluorene-containing polymers are those with high carrier mobility as measured by standard techniques such as time-of-flight experiments as described by Van der Auweraer, *et al.* in Advanced Materials, Vol. 6, p. 199, 1994. More preferred are fluorene-containing polymers with non-dispersive carrier transport behavior, for example, poly(9,9-dioctylfluorene-2,7-diyl) described by Redecker, *et al.* in Applied Physics Letters, Vol. 73, p. 1565, 1998. Also preferred, are alternating fluorene copolymers with tertiary aromatic amines,

as described in the above referenced '469 and '187 United States Patent Applications. These polymers have carrier mobility of at least  $1 \times 10^{-4}$  cm<sup>2</sup>/volt - second.

The semiconductor layer 15 may comprise a mixture of polymers. The polymer of the semiconductor layer 15 can be homogeneous or phase separated; it may also be amorphous, semicrystalline or liquid crystalline in morphology. The polymer may also be aligned in the liquid crystalline state for enhanced carrier mobility as described by Grell, *et al.* in Advanced Materials, Vol. 9, p. 798, 1997. The thickness of the semiconductor layer 15 is not critical and may vary, for example, from 1 nm to 1000 nm, preferably 10 nm to 500 nm, most preferably 20 nm to 100 nm.

The source 20 and the drain 21 can then be deposited, for example, through a mask by sputtering or thermal evaporation in vacuum. Preferred materials for the source 20 and the drain 21 are gold, silver, or aluminum. A negative bias applied to the gate causes the formation of a conduction channel in the semiconductor layer 15 at or near its interface with the insulator 11. A current flows from the source 20 to drain 21 when the latter is made negative relative to the former. The MISFET of this invention are characterized by high on-off ratio and field effect mobility.

CLAIMS

1. A field effect transistor, comprising:

(a) an insulator layer, the insulator layer being an electrical insulator, the insulator layer having a first side and a second side;

5 (b) a gate, the gate being an electrical conductor, the gate being positioned adjacent the first side of the insulator layer;

(c) a semiconductor layer, the semiconductor layer comprising a polymer, at least ten weight percent of the monomer units of the polymer being selected from a 9-substituted fluoreno unit and a 9,9-substituted fluoreno unit, the semiconductor layer having a  
10 first side, a second side, a first end and a second end, the second side of the semiconductor layer being adjacent the second side of the insulator layer;

(d) a source, the source being an electrical conductor, the source being in electrical contact with the first end of the semiconductor layer; and

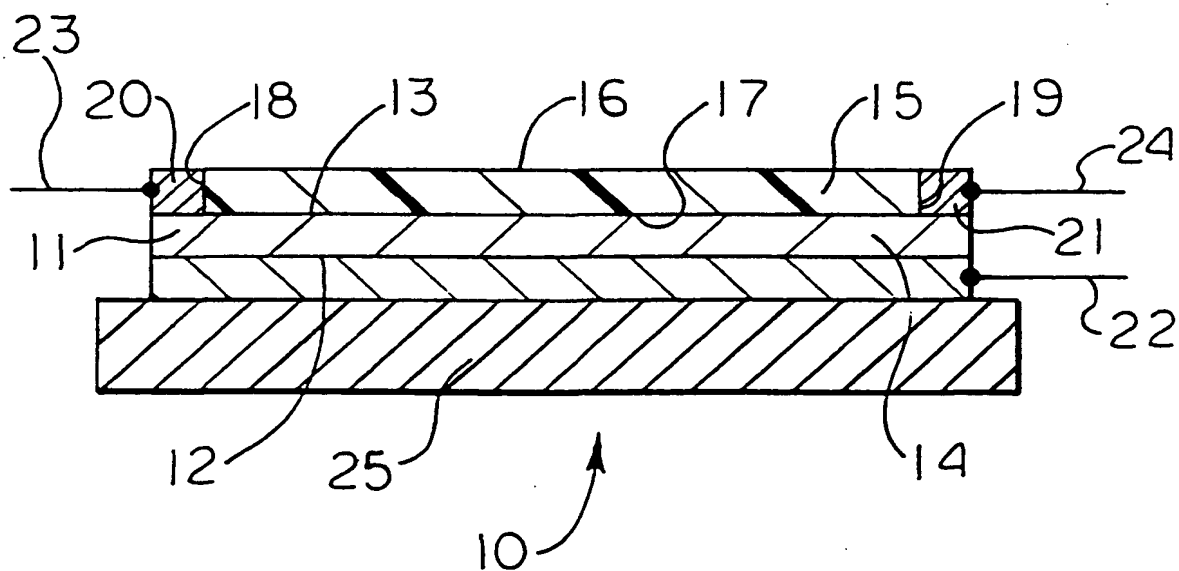
(e) a drain, the drain being an electrical conductor, the drain being in electrical  
15 contact with the second end of the semiconductor layer.

2. The transistor of Claim 1, wherein the semiconductor layer consists essentially of a polymer, at least ten weight percent of the monomer units of the polymer being selected from a 9-substituted fluorene unit and a 9,9-substituted fluorene unit.

3. The transistor of Claim 1 or 2, wherein at least 20 weight percent of the  
20 monomer units of the polymer are selected from a 9-substituted fluorone unit and a 9,9-substituted fluorene unit.

4. The transistor of Claim 1 or 2, wherein at least 30 weight percent of the monomer units of the polymer are selected from a 9-substituted fluorene unit and a 9,9-substituted fluorene unit.

25 5. The transistor of Claim 1, 2, 3 or 4, wherein the semiconductor layer is in direct contact with the insulator layer and wherein the gate is in direct contact with the insulator layer.

*Fig. 1*

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/30612

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 528 662 A (TOKYO SHIBAURA ELECTRIC CO) 24 February 1993 (1993-02-24) column 4, line 9 - line 23	1-5
A	EP 0 450 862 A (TOKYO SHIBAURA ELECTRIC CO) 9 October 1991 (1991-10-09) column 6, line 1 - line 40 -/-	1-5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

19 April 2000

Date of mailing of the international search report

02/05/2000

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Königstein, C

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/30612

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	REDECKER M ET AL: "NONDISPERSIVE HOLE TRANSPORT IN AN ELECTROLUMINESCENT POLYFLUORENE" APPLIED PHYSICS LETTERS,US,AMERICAN INSTITUTE OF PHYSICS. NEW YORK, vol. 73, no. 11, 14 September 1998 (1998-09-14), pages 1565-1567, XP000784075 ISSN: 0003-6951 cited in the application the whole document	1-4
A	UEHARA K ET AL: "CONTROL OF ELECTRON TRANSFER DIRECTION IN AN ORGANIC TWO-LAYER DIODE BASED ON A LIGHTLY-DOPED POLY(3-METHYLTHIOPENE)/9-FLUORENONE DERIVATIVES JUNCTION" THIN SOLID FILMS,CH,ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 266, no. 2, 1 October 1995 (1995-10-01), pages 263-266, XP000622867 ISSN: 0040-6090 the whole document	1
P,X	REDECKER M ET AL: "HIGH MOBILITY HOLE TRANSPORT FLUORENE-TRIARYLAMINE COPOLYMERS" ADVANCED MATERIALS,DE,VCH VERLAGSGESELLSCHAFT, WEINHEIM, vol. 11, no. 3, 11 February 1999 (1999-02-11), pages 241-246, XP000803283 ISSN: 0935-9648 the whole document	1-4

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/30612

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0528662 A	24-02-1993	JP 5048094 A	26-02-1993
		DE 69205766 D	07-12-1995
		DE 69205766 T	25-04-1996
		KR 9615783 B	21-11-1996
		US 5355235 A	11-10-1994
EP 0450862 A	09-10-1991	JP 4211229 A	03-08-1992
		US 5155566 A	13-10-1992

**THIS PAGE BLANK (USPTO)**